THE UNIVERSITY of EDINBURGH

Edinburgh Research Explorer

Structural and theoretical investigations of short hydrogen bonds: Neutron diffraction and plane-wave DFT calculations of urea-phosphoric acid

Citation for published version:
Morrison, C & Wilson, CC 2002, 'Structural and theoretical investigations of short hydrogen bonds: Neutron diffraction and plane-wave DFT calculations of urea-phosphoric acid', *Chemical Physics Letters*, vol. 362, no. 1-2, pp. 85-89. https://doi.org/10.1016/S0009-2614(02)00952-1

Digital Object Identifier (DOI):
10.1016/S0009-2614(02)00952-1

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Peer reviewed version

Published In:
Chemical Physics Letters

Publisher Rights Statement:
Copyright © 2002 Elsevier Science B.V. All rights reserved.

General rights
Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

OPEN ACCESS

Download date: 07. May. 2023

This is the peer-reviewed author's version of a work that was accepted for publication in Chemical Physics Letters. Changes resulting from the publishing process, such as editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version is available at:
http://dx.doi.org/10.1016/S0009-2614(02)00952-1

Cite as:
Morrison, C., & Wilson, C. C. (2002). Structural and theoretical investigations of short hydrogen bonds: Neutron diffraction and plane-wave DFT calculations of urea-phosphoric acid. *Chemical Physics Letters*, 362(1-2), 85-89.

Manuscript received: 11/02/2002; Revised: 10/06/2002; Article published: 01/08/2002

Structural and theoretical investigations of short hydrogen bonds: Neutron diffraction and plane-wave DFT calculations of urea–phosphoric acid**

Chick C. Wilson[1] and Carole A. Morrison[2]

[1]ISIS Facility, CLRC Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK.

[2]EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK.

[*]Corresponding author; e-mail: c.c.wilson@rl.ac.uk, fax: +01235-445-720

[**]This work was partly funded by EPSRC Grant GR/R04690 (to CCW). CAM gratefully acknowledges the award of a Royal Society University Research Fellowship.

Abstract:
Low temperature neutron diffraction and high level computational methods have been applied to investigate the short hydrogen bond in urea‑phosphoric acid. It is found that isolated molecule calculations predict a `normal' O‑H···O hydrogen bond, in strong disagreement with the very short, 3c‑4e hydrogen bond found from the neutron diffraction. Extending these calculations into a periodic environment using plane-wave DFT methods give much improved agreement with experiment, with a much shorter, stronger hydrogen bond, and significant elongation of the O‑H `covalent' bond.

1. Introduction

The study of relatively simple organic molecules is a vital source of information regarding the underlying physical forces that hold these molecules together. In particular, in the solid state, the study of crystal structures yields information on the intermolecular forces. The intermolecular hydrogen bonding which is so often present in such systems plays an important role in forming anisotropic interactions, and, for example, the hydrogen transfer through hydrogen bonds between molecules enables charge and energy transfer in solid chemical and biological systems and has widespread implications for issues as diverse as ferroelectrics, electrochemical processes and enzyme action [1].

In particular, we focus here on the long standing issue of the geometry, proton position and shape of the potential well in very short, strong hydrogen bonds. In general the formation of a D-H···A hydrogen bond (HB) is expected to change the potential energy surface for the D-H group from a single minimum to a symmetric or asymmetric double minimum. This simple picture, however, does not hold for very short, strong hydrogen bonds, which in the case of O-H-O HB typically have O···O distances in the range 2.4 – 2.55Å. Such strong HB have been subjected to much analysis by single crystal neutron diffraction [2], as they are often found to be close to symmetric, with consequently elongated D-H "covalent" bonds and shorter H···A "non-bonded" separations. Such a situation can be described as exhibiting three-centre, four-electron (*3c, 4e*) bonding.

Neutron single crystal diffraction provides a powerful method of examining proton positions and behaviour in such cases. In particular, the technique allows accurate refinement of the positions and anisotropic atomic displacement parameters (ADPs, thermal parameters) of the hydrogen atoms in such short HB, yielding information on the interatomic potential. Neutron diffraction studies have in many cases supported the view that the potential energy curve becomes flattened close to its minimum, and the proton vibrates anharmonically in this curve [2].

However, we note also that the positions of the hydrogen atoms are also strongly affected by the crystalline environment, and recent studies have shown that the

apparent position of the hydrogen atom in short HB can vary as a function of temperature [3 – 6] and also possibly pressure [7].

The 1:1 adduct of urea and phosphoric acid (UPA) exhibits such a short HB and it is this structure we examine here. The chemical and structural interest in materials such as UPA lies in the wide range of hydrogen bonding exhibited when urea is used as a complexing agent for organic acids. For example, the degree of hydrogen atom "transfer" from the acid to the urea compound in such complexes can vary from close to zero, for example in urea-oxalic acid (2:1) [8], to almost complete, in urea-nitric acid, for example [9]. UPA shows a situation intermediate between the two, with a near-symmetric O-H-O arrangement evident at room temperature [10, 3, 4].

2. Complementary structural and computational approach

The descriptions of the behaviour of protons in such short HB and very reliant on a fuller understanding of the shape of the HB potential, information about which is necessarily limited from diffraction data. We have therefore carried out high level quantum chemical calculations on the UPA system, to complement neutron diffraction measurements and help shed light on this potential.

2.1 Low temperature neutron diffraction

In order to provide an accurate close to 0K experimental structure to be used to initialise the subsequent calculations, the structure of UPA was re-determined, at 15K, using single crystal neutron diffraction on the SXD instrument at the ISIS Spallation Neutron Source [11, 12]. The resulting structure is shown in Figure 1, with selected bond lengths and angles given in Table 1.

Figure 1

Table 1

2.2 Isolated molecule calculations

A graded series of *ab initio* molecular orbital calculations were performed on an isolated dimer unit of UPA, with the starting geometry obtained from the low temperature neutron diffraction structure determination. A vibrational frequency calculation confirmed the optimised structure obtained as a minimum (all force constants positive). All calculations were carried out using the GAUSSIAN98 package [15], using a Linux 800 MHz dual-processor PC.

The basis sets used in these calculations ranged from 6-31G* to 6-311++G* with HF and B3PW91 levels of theory; the results obtained from the highest level calculation are presented in Table 1. From this it can be seen that isolated molecule calculations do not reproduce the geometric features of interest in this complex. In particular, the description of the O-H-O HB linkage is not at all in agreement with that determined experimentally. The highest level calculation produces a HB geometry with an O···O separation of 2.61 Å, which is indicative of a normal length/strength hydrogen bond. This is further supported by the O-H and H···O separations of 1.004 and 1.604 Å (Δ = 0.6 Å) which are of the normal covalent and non-bonded values typically found in medium-strength hydrogen bonds. This is in strong disagreement with the experimentally determined short hydrogen bond in UPA, with values at 15 K of O-H, 1.158(3) Å, H···O, 1.267(3) Å, and O···O separation of 2.420(2) Å. Clearly any conclusions drawn about the HB potential on the basis of these calculations would be inadequate.

2.3 Plane-wave DFT calculations

In order to investigate this complex further, and in particular to investigate the intermolecular HB interaction, a set of plane-wave (periodic) DFT calculations were also carried out on the UPA complex. By incorporating the periodic nature of the crystal lattice into the calculations, it is hoped to reproduce the molecular structure in the crystal more accurately.

Calculations were undertaken using the VASP 4.4 simulation code [16] on a Linux 800 MHz duel-processor PC. A generalised gradient approximation (PW91) was used

for the exchange and correlation potential [17]. The wavefunction was generated using a series of pseudopotentials (in effect to describe the atomic cores) and delocalised plane waves (in effect describing the valence region) expressed at an energy cut-off of 396 eV. Integrations over the symmetrised Brillouin zone were performed using one k-point positioned at the Γ-point.

Calculations were performed on a 1 x 1 x 1 lattice, with starting values for atomic coordinates and lattice vectors taken from the low temperature crystal structure determination (*i.e.* 128 atoms, space group Pbca, eight equivalent urea-phosphoric acid dimers in the unit cell). The first set of calculations established the volume of the periodic cell giving rise to the lowest lattice energy, with subsequent fixed-volume calculations alternating between the optimisation of unit cell parameters and atomic positions until convergence was achieved (*i.e.* forces to within 0.020 eV.Å^{-1}, change in energy per atom to within 1.5 x 10^{-5} eV); the results are shown in Table 1.

The first point to note for the optimised lattice obtained relates to the unit cell parameters: the cell volume is marginally bigger (+3%), but this signifies an increase in the three lattice vectors of no more than 0.15 Å. The experimental geometry is far better simulated by the plane-wave DFT calculations than by the isolated molecule approach. In general plane-wave DFT reproduced all intramolecular bond distances to within 0.02 Å (some to well within 0.01 Å) and angles to within 1º, compared to 0.03-0.05 Å and 1-5º agreement for bond distances and angles in the isolated molecule simulations. For the intermolecular HB in the complex, plane-wave DFT predicts a short, strong HB with O···O separation of 2.42 Å, and an asymmetry of Δ = 0.22 Å, reflecting the significant elongation of the O-H (1.105 Å) and shortening of H···O (1.329 Å) distances. A criticism that can be fairly levied at current DFT functionals is the failure to model dispersive interactions. However, as the short O···O contact is modelled to within 0.01 Å of the experimental value, it is reasonable to assume that the bond is strongly covalent in nature, and that any component of the hydrogen bond attributed to instantaneous dipoles is likely to be very small. This is in agreement with the classification system for hydrogen bonds published by Jeffrey [18]. While still representing a greater asymmetry than that found in the crystal structure, (Δ = 0.11 Å), the plane-wave DFT calculations clearly do give a better

description of the known structure in the crystal environment (Figure 2), and consequently the deductions from these calculations may yield useful insight into the nature and behaviour of the HB potential.

Figure 2

4. Conclusions

It is clear that the 0K (*i.e.* equilibrium) plane-wave DFT calculations produce an optimised molecular geometry for the UPA complex which largely reproduces the low temperature experimentally determined values. In particular, the short, strong O-H-O HB is reasonably well reproduced, vital if we are to use computational methods to augment our neutron diffraction data. Isolated molecule calculations are notably unsuccessful in producing the UPA geometry.

To the best of our knowledge this is the first application of plane-wave DFT calculations to such a short, strong intermolecular *3c,4e* hydrogen bond and these initial observations are thus very significant. The promise of the plane-wave DFT approach in understanding this system will be explored further in two ways: the PES of the 0K structure in the region around the HB will be mapped out by single point calculations, and further PW-DFT optimisations will be carried out on the structure at higher temperatures via molecular dynamics simulation - the latter in particular is computationally intensive and time-consuming. In this way we hope to map out computationally the observed proton migration in this material [3, 4] and ultimately understand how this may be driven by the underlying potential.

5. Acknowledgements

This work was partly funded by EPSRC grant GR/R04690 (to CCW). CAM gratefully acknowledges the award of a Royal Society University Research Fellowship.

6. References

[1] G. Zundel, Adv. Chem. Phys. 111 (2000) 1.

[2] G.A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, New York, 1997; C.C. Wilson, *Single Crystal Neutron Diffraction from Molecular Materials*, pp. 211-229, World Scientific, Singapore, 2000.

[3] C.C. Wilson, Acta Cryst. B57 (2001) 435.

[4] C.C. Wilson, K. Shankland, N. Shankland, Z. Krist. 216 (2001) 303.

[5] T. Steiner, I. Majerz, C.C Wilson, Angew. Chem. Int. Ed. Engl. 40 (2001) 2651.

[6] J.A.K. Howard, personal communication

[7] C.C. Wilson, in preparation (2002).

[8] G.J van Hummel, R.B. Helmholdt, Acta Cryst. C47 (1991) 213.

[9] J.E. Worsham, W.R. Busing, Acta Cryst. B25 (1969) 572.

[10] E.C. Kostansek, W.R. Busing, Acta Cryst. B28 (1972) 2454.

[11] C.C. Wilson, In *Neutron Scattering Data Analysis 1990* (Ed. M.W. Johnson), p. 145-163. IoP Conference Series vol. 107, Adam Hilger, Bristol, 1990.

[12] C.C. Wilson, J. Mol. Struct. 405 (1997) 207.

[13] C.K. Johnson, *ORTEP, Thermal Ellipsoid Plotting Program*, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, USA, 1971. Program version used: ORTEP-III by C.K. Johnson & M.N. Burnett, implemented as ORTEP 3 for Windows [15].

[14] L.J. Farrugia, J. Appl. Cryst. 30 (1997) 565.

[15] *Gaussian 98* Revision A.7, Gaussian, Inc., Pittsburgh PA, 1998.

[16] G. Kresse, J. Furthmueller, Comp. Mater. Sci. 6 (1996) 15.

[17] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, D.J. Singh, C. Fiolhais, Phys. Rev. B46 (1992) 5571.

[18] G.A. Jeffrey, *An introduction to Hydrogen Bonding*, Oxford University Press, Oxford, 1997.

Table 1 - Experimental and calculated parameters for urea-phosphoric acid

Parameter	Neutron Diffraction (15 K)	Gaussian (rb3pw91/ 6-311++G*)	Calculated (plane-wave DFT) (0 K)
Lattice			
a	17.401	-	17.529
b	7.428	-	7.494
c	8.903	-	9.025
V	1150.8	-	1185.6
Structural			
Urea			
*r*C(1)-O(5)	1.284	1.235	1.313
*r*C(1)-N(2); *r*C(1)-N(1)	1.323; 1.325	1.358; 1.370	1.326; 1.330
∠O(5)-C(1)-N(2), ∠O(5)-C(1)-N(1)	121.0; 118.1	123.2; 120.5	120.5; 117.5
Phosphoric acid			
*r*P(1)-O(4)	1.513	1.571	1.522
*r*P(1)-O(2)	1.511	1.468	1.536
*r*P(1)-O(3); *r*P(1)-O(1)	1.555; 1.562	1.602; 1.648	1.578; 1.580
∠O(4)-P(1)-O(2); ∠O(4)-P(1)-O(3); ∠O(4)-P(1)-O(1)	113.4; 111.6; 105.6	122.9; 101.7; 100.8	113.4; 112.0; 106.1
Urea-phosphoric acid linkage			
*r*O(5)-H(4)	1.158	1.604	1.105
*r*O(4)-H(4)	1.267	1.004	1.329
∠C(1)-O(5)-H(4)	116.1	125.3	114.7
∠P(1)-O(4)-H(4)	125.2	119.5	125.7
τ P(1)-O(4)-O(5)-C(1)	28.7	62.9	36.2
Computational			
E / eV	-	-	-775.08195
E / Hartrees	-	-869.3609198	-

FIGURE CAPTIONS

	O5-H4	O5...O4	H4…O4
Neutron, 15K	1.158(4)Å	2.416(2)Å	1.267(4)Å
Isolated molecule	1.604Å	2.60Å	1.004Å
Plane-wave DFT	1.105Å	2.42Å	1.329Å

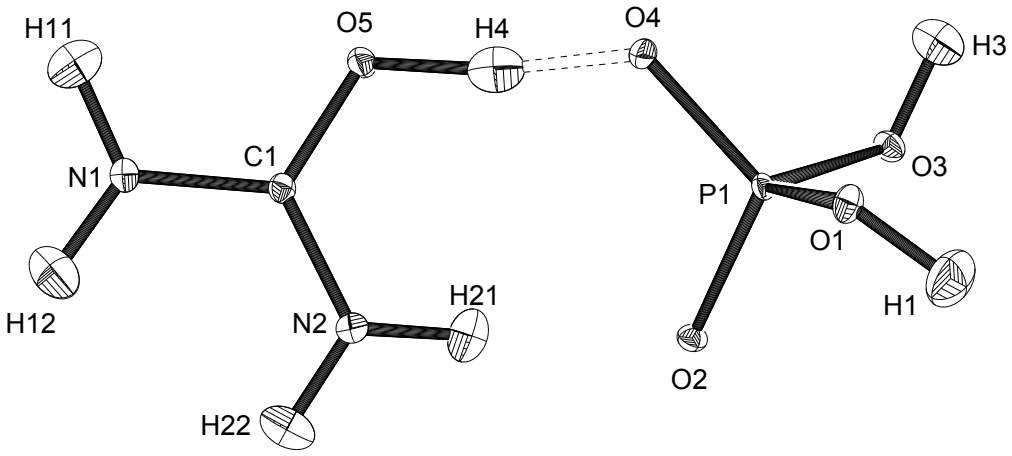

Figure 1 – ORTEP [14, 15] view of the structure of urea-phosphoric acid, determined by single crystal neutron diffraction at 15K, with the ellipsoids illustrating the anisotropic atomic displacement parameters plotted at the 50% probability level. Also indicated is the geometry of the short, strong hydrogen bond as observed by low temperature neutron diffraction and calculated by the high level isolated molecule *ab initio* and plane-wave DFT methods described in the text. The dramatic improvement in describing this system on moving from isolated molecule to periodic DFT calculations is clear.

To come still….

Figure 2 – The crystal packing of urea-phosphoric acid and the intermolecular environment of the short, strong hydrogen bond in urea-phosphoric acid.